



Intrinsic reactivity of alkaline and alkaline-earth metal oxide catalysts for oxidation of soot

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ABSTRACT

The reactivity of selected alkaline (Na, K, Cs) and alkaline-earth (Ca, Ba, Mg) oxide catalysts in the oxidation of a model soot sample (Printex U) is investigated in this study. With the aim of obtaining information about the intrinsic reactivity of these elements, samples have been prepared in which the active elements have been directly deposited on the soot ("full contact" conditions). In this way the reactivity of the catalytic elements is not controlled by the type of contact with the soot. It is found that the combustion of soot is greatly enhanced by the presence of either alkaline or alkaline-earth oxides, with Cs and Mg exhibiting the highest and the lowest activity, respectively. Notably, the reactivity in the soot combustion is found to nicely correlate with the electropositivity of the investigated metal ions, in line with literature indications pointing out the relevance of the electron-donor characteristics of the active elements. The correlation between electropositivity and activity in the soot combustion is not apparent in the absence of a close contact, i.e. under loose contact conditions. Under these conditions it is suggested that the catalytic activity is governed by the mobility of the surface species, which favors the soot–catalyst contact. Accordingly the poor performances observed in the case of the alkaline-earth metal oxides suggest for these elements a poor mobility of the active surface species, as opposite to alkaline oxide based catalysts showing a high reactivity even under loose contact conditions.

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1. Introduction

The diesel engines market has been significantly increased in recent years in Europe. The reasons of such spreading are essentially related to the good driving characteristics of the modern diesel engines, and to their lower fuel consumptions (up to 30%) if compared to the traditional gasoline power units. However, diesel exhausts have been blamed for urban and global air pollution due to the emissions of nitrogen oxides (NO_x) and of particulate matter (PM or soot). For these reasons, more stringent regulations to reduce pollutants emissions from diesel engines (and from Otto engines as well) are progressively coming in force. The recently adopted Euro V rules requires for light-weight motor vehicles (i.e. with a weight up to 2500 kg) a fivefold decrease of soot emissions if compared to the previous Euro IV regulations, from 0.025 g/km (Euro IV) to 0.005 g/km (Euro V). An even more drastic reduction is expected for NO_x with the coming Euro VI rules.

Remarkable efforts are being made by car manufacturers to explore innovative technologies that may allow the reduction of polluting emissions from diesel engines, and in particular of soot. The development of new and more efficient engines equipped with

sophisticated diesel injection systems and with advanced combustion technologies has impacted the reduction of pollutant emissions, but after-treatment technologies must be applied as well to comply with the strict emissions standards. At present, the common after-treatment technology used to reduce soot emissions consists in the employment of diesel particulate filters (DPF), which traps the soot particles contained in the exhaust stream. These filters must be periodically regenerated, generally by a temperature increase of the filter which leads to the oxidation of the soot particles. The temperature increase is generally attained by combustion on the filter of extra-fuel injected in the exhausts; for this reason the filter might be catalyzed (generally with noble metals) to favor the fuel combustion. The catalytic layer deposited onto the filter may also favor the soot oxidation. Different kinds of catalysts have been proposed for this purpose, including single and mixed metal oxides, perovskite- and spinel-type oxides [1–5]. Many catalyst formulations include alkali metal oxides, which have been claimed to bring substantial benefits for soot oxidation [6–11]. It has been suggested that alkali oxides may favor the reaction through the formation of low melting point compounds, or of eutectics with other catalyst components, thus improving the surface mobility of the active species and hence favoring the soot–catalyst contact [12–14] which has been claimed as a key factor in the oxidation of soot with oxygen [2,3,11,15]. Among alkalis, the catalytic activity of potassium salts and containing mixed oxides

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has been considered by several authors for the combustion of carbonaceous materials [11,13,14,16,17]. The use of potassium has also been included in catalyst formulations for the simultaneous NO_x and soot removal according to the so-called Diesel Particulate NO_x Removal (DPNR) concept recently proposed by Toyota [18]. It has been shown in the DPNR technique that K-containing catalytic materials are characterized by similar DeNO_x activity but higher soot combustion performances with respect to analogous Ba-based samples [19–21]. Besides K, also Cs-based molten salts have been indicated by Moulijn and co-workers [12,22,23], as promising catalysts for soot oxidation due to formation of mobile liquid-phases.

In order to provide further insights on the role of alkali and alkaline-earth metal oxides in the combustion of soot, in this work a systematic analysis has been carried out aiming to point out the intrinsic reactivity in the reaction of alkaline and alkaline-earth oxides. In the investigation selected alkaline (Na, K and Cs) and alkaline-earth (Mg, Ca and Ba) oxide species have been considered, which are commonly used in De-soot and coupled De-soot/De-NO_x catalytic formulations. In particular, aim of the present work is to clarify whether these compounds own a specific reactivity in the oxidation of soot or simply behave as promoters or doping materials. To our best knowledge, a systematic investigation aiming at clarifying the intrinsic reactivity of these species has never been reported in the literature.

The intrinsic reactivity of the selected active elements has been evaluated through the preparation of samples in which an intimate contact is provided between the investigated catalytic elements and the soot particle. This has been accomplished by direct impregnation of the soot with aqueous solutions of the catalytic elements: in this way the reactivity of the catalytic elements is not controlled by the type of contact with the soot. The samples prepared according to this procedure have been indicated hereafter as “full contact”. For comparison purpose, a series of samples has also been prepared in which the alkaline and alkaline-earth oxide catalytic systems have been supported on an alumina support and then gently mixed with the soot. In this case a “loose contact” is obtained between the soot and the catalyst samples, and the reactivity of the same elements when not in close contact with the soot could be pointed out. The obtained results could be relevant for Fuel Borne Catalyst (FBC) applications as well, when suited additives are added to the fuel in order to promote the soot oxidation during regeneration of DPFS.

2. Experimental

2.1. Catalysts preparation and characterization

The full contact samples have been prepared by direct impregnation of soot with aqueous solutions of the selected alkaline (i.e. Na, K and Cs) and alkaline-earth (i.e. Mg, Ca and Ba) acetate salts. The selected metal loading was 1.1 mmol/g_{soot} for all samples. Printex U (Degussa) was used as model soot, whose properties have been well assessed (e.g. in Refs. [24–26]). After impregnation, all the samples have been dried at 100 °C in air for 2 h.

The γ-Al₂O₃ supported alkaline and alkaline-earth metal oxide samples, i.e. Na/, K/, Cs/, Mg/, Ca/ and Ba/Al₂O₃, have been prepared starting from a commercial alumina support (Versal 250 from UOP) previously calcined at 700 °C. This support has been impregnated with aqueous solutions of alkaline and alkaline-earth acetates. The metal loading was 1.4 mmol/g_{cat} for all samples. The powders have been dried at 80 °C in air and calcined at 500 °C in air for 5 h after impregnation. The catalysts have been characterized by XRD (Philips PW 1050/70), surface area and pore size distribution (Micromeritics TriStar 3000 instrument). Catalyst-soot mixtures have been prepared by gently mixing in a vial

the catalyst powder (sieved at 70–100 μm) with the soot, thus realizing a loose contact. A catalyst/soot ratio of 9/1 w/w has always been employed.

2.2. Reactivity tests

The reactivity tests have been performed in a flow-reactor equipment consisting of a quartz tube reactor (7 mm I.D.) connected to a mass spectrometer (Thermostar 200, Pfeiffer Vacuum) and to a micro GC (Agilent 300A) for the on-line analysis of the gases exiting the reactor. The reactivity of all the samples (bare soot and catalytic samples with full and loose contact) has been investigated under temperature programming (Temperature Programmed Oxidation, TPO) and under isothermal conditions as well. In the case of TPO runs, the soot-catalyst systems have been heated from RT to 800 °C @ 15 °C/min under a He/O₂ flow (3% O₂ v/v, total flow 100 ml/min at 0 °C and 1 atm). Three different parameters have been derived in order to evaluate the activity of the catalysts in the soot combustion: *T*_{on} (ignition temperature, i.e. the temperature at which the CO_x concentration exceeds 300 ppm), *T*_{max} (the temperature corresponding to the maximum in the TPO profile) and *T*₅₀ (i.e. the temperature required to reach 50% soot conversion). Formation of CO and CO₂ was always observed during the TPO run; the CO₂ selectivity (*S*_{CO₂}) has been calculated as $S_{CO_2} = n_{CO_2} / (n_{CO_2} + n_{CO})$, where *n*_{CO₂} and *n*_{CO} are the moles of CO₂ and CO produced during the TPO run, respectively. Replicated runs show a good reproducibility of the TPO runs, with changes in *T*_{max} within the range of about 10–20 °C.

Combustion activity has been analyzed under isothermal conditions as well. In a typical run, the catalyst sample was heated at 400 °C in He + 3% v/v O₂ + 1% v/v H₂O and maintained at this temperature for 2 h, while monitoring CO₂ evolution. Then a TPO experiment (up to 800 °C) was carried out to quantify the residual amount of soot.

Before each activity test the catalyst/soot mixture was heated at 500 °C in He to desorb and/or decompose any weakly adsorbed species. In each test 10 mg of full contact samples have been used, diluted 1/5 w/w with quartz powder, or 66 mg of the 9/1 catalyst/soot loose contact mixture.

3. Results

3.1. Catalysts characterization

The surface area (*S*), pore volume (*V*_p) and average pore diameter (*d*_p) of the investigated catalytic systems are listed in Table 1. The specific surface area of the bare γ-Al₂O₃ support is near 200 m²/g. Lower surface areas have been determined for both the alkaline and alkaline-earth-containing samples. The surface area contraction is accompanied by a slight reduction of the pore volume, with a similar trend. For all samples the pore diameter is in the range 150–180 Å.

The XRD spectra of the Al₂O₃-supported samples (not shown for brevity) show the typical pattern of the microcrystalline γ-Al₂O₃ (JCPDS 10-425). Reflects related to alkaline- or alkaline-earth-

Table 1

Material characterization: surface area, pore volume and average pore diameter.

Catalytic systems	<i>A</i> _s [m ² /g]	<i>V</i> _p [cm ³ /g]	<i>d</i> _p [Å]
γ-Al ₂ O ₃	207.4	0.96	153
Na/Al ₂ O ₃	170	0.90	181
K/Al ₂ O ₃	180	0.82	152
Cs/Al ₂ O ₃	161	0.77	167
Mg/Al ₂ O ₃	172	0.85	164
Ca/Al ₂ O ₃	154	0.78	168
Ba/Al ₂ O ₃	136	0.65	167

carbonate phases have been detected only in the case of the Ca- (CaCO_3 , JCPDS 72-1937) and Ba- (BaCO_3 monoclinic, JCPDS 78-2057, and orthorhombic Whiterite, JCPDS 5-378) containing samples. For all the other samples no other crystalline phases were detected, thus suggesting that the deposited alkaline and alkaline-earth metal oxide phases are mainly amorphous.

All the full contact systems and the bare soot do not show any reflects at the XRD analysis.

4. Reactivity studies

4.1. "Full contact" systems

The samples prepared by direct impregnation of the soot ("full contact" samples) are representative of a very intimate contact between the soot and the catalytic elements. In these conditions the intrinsic reactivity of the active elements (alkaline and alkaline-earth oxides species, i.e. Na, K, Cs, Mg, Ca and Ba) can be measured. Fig. 1A and C show the CO_x ($\text{CO}_2 + \text{CO}$) evolution obtained during TPO experiments carried out over the various samples (Na, K, Cs in Fig. 1A, and Mg, Ca, Ba in Fig. 1C). The results obtained in the case of the un-catalyzed soot are also shown for comparison purposes.

In Fig. 1B and D the same data are plotted in terms of soot conversion vs. temperature and the values of T_{50} are also shown. In all cases the O_2 consumption profiles (not shown) are always symmetrical to those of CO_x . The temperature onset T_{on} for the un-catalyzed soot oxidation is close to 480°C , whereas the peak maximum (T_{max}) is seen at 710°C . At 690°C 50% of the soot initially loaded is combusted, and the soot oxidation is completed around

780°C . The amounts of CO and CO_2 produced in this case are nearly the same, and this results in a CO_2 selectivity (S_{CO_2}) near 54%.

Significant changes in the TPO spectra are observed when the catalytic elements are deposited onto the soot. In fact in all cases (with the only exception of Mg) both the ignition temperature and the peak temperature for soot oxidation significantly decrease as compared to those of the un-catalyzed soot sample (see Fig. 1A and C). The Mg-containing sample, on the other hand, shows a very poor reactivity if compared to the other samples. Among the investigated alkaline oxide systems (see Fig. 1A and B) the lowest initial combustion temperature is observed for the Cs- and K-doped soot systems. In these cases the onset temperature T_{on} is monitored near 250 and 260°C , respectively, i.e. more than 200°C below that of the un-catalyzed soot system. After ignition, soot combustion proceeds rapidly; the maximum peaks are observed near 450°C , i.e. about 260°C below that of the un-catalyzed soot. Also the CO_2 selectivity is increased by the presence of cesium and potassium; CO_2 selectivity is 90% for the Cs/soot and 94% for the K/soot. The Na-doped soot also exhibits a low combustion onset temperature (near 280°C), very close to that of K/ and Cs/soot, but after ignition the soot combustion proceeds slightly slower than in the case of the Cs- and K-containing samples.

The alkaline-earth oxide systems (Fig. 1C and D) show much higher differences in their activity. Indeed whereas a noticeable drop in the ignition temperature (with respect to the bare soot) is evident for the barium containing sample ($T_{\text{on}} = 295^\circ\text{C}$), the Mg containing system shows a very poor reactivity ($T_{\text{on}} = 440^\circ\text{C}$). The presence of Ca (Ca/soot system) enhances soot oxidation ($T_{\text{on}} = 350^\circ\text{C}$), although the soot oxidation activity of this alkaline-earth oxide is lower than that of Ba.

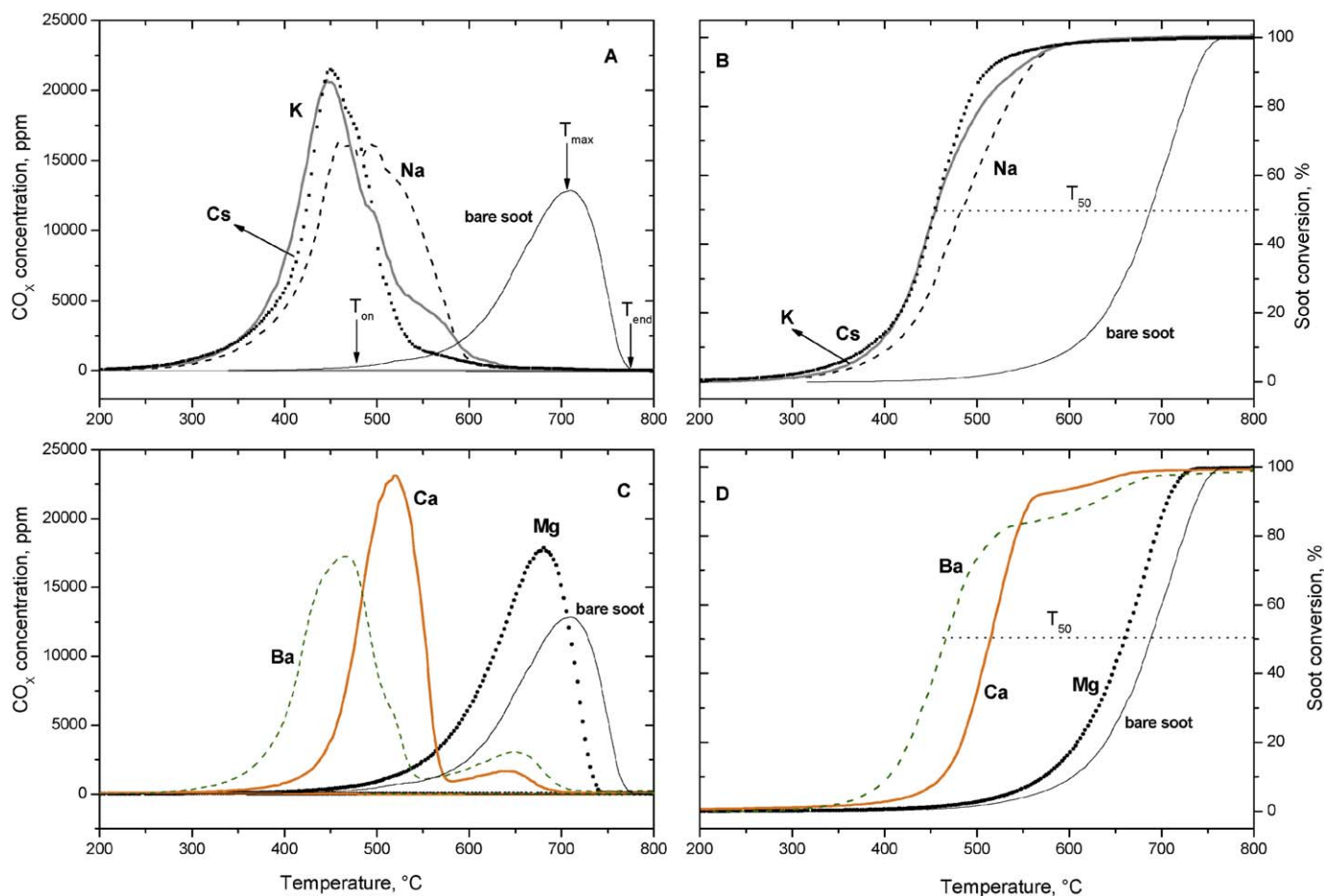


Fig. 1. Results of TPO experiments in O_2 (3% v/v) + He in terms of CO_x concentration (A and C) and in terms of soot conversion (B and D) over full contact systems.

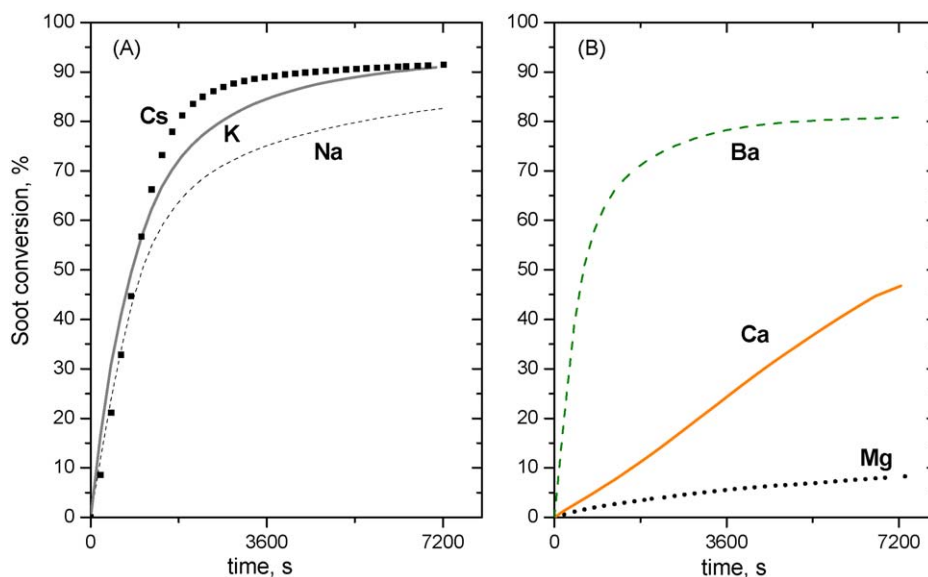


Fig. 2. Results of isothermal oxidation in the presence of O_2 (3% v/v) + H_2O (1% v/v) + He in terms of soot conversion over full contact systems: (A) alkaline metal oxide; (B) alkaline-earth metal oxide.

The CO_2 selectivity is also increased in the case of Ba and Ca if compared to the bare soot, and values near 95% and 72% have been measured in these cases, respectively. On the other hand, the presence of Mg does not increase significantly the CO_2 selectivity ($S_{CO_2} = 58\%$).

The reactivity of alkaline/ and alkaline-earth/soot systems towards soot oxidation has also been considered under isothermal

condition (400 °C), and results are shown in Fig. 2 in terms of soot conversion vs. time-on-stream. All the soot samples doped with alkaline metal oxides show significant activity at the selected temperature, in line with the results of TPO experiments carried out over the same samples (Fig. 2A). The following order of reactivity is observed: $Cs > K > Na$. In fact after 1 h the soot conversion over these samples approaches 90%, 85% and 75%, respectively.

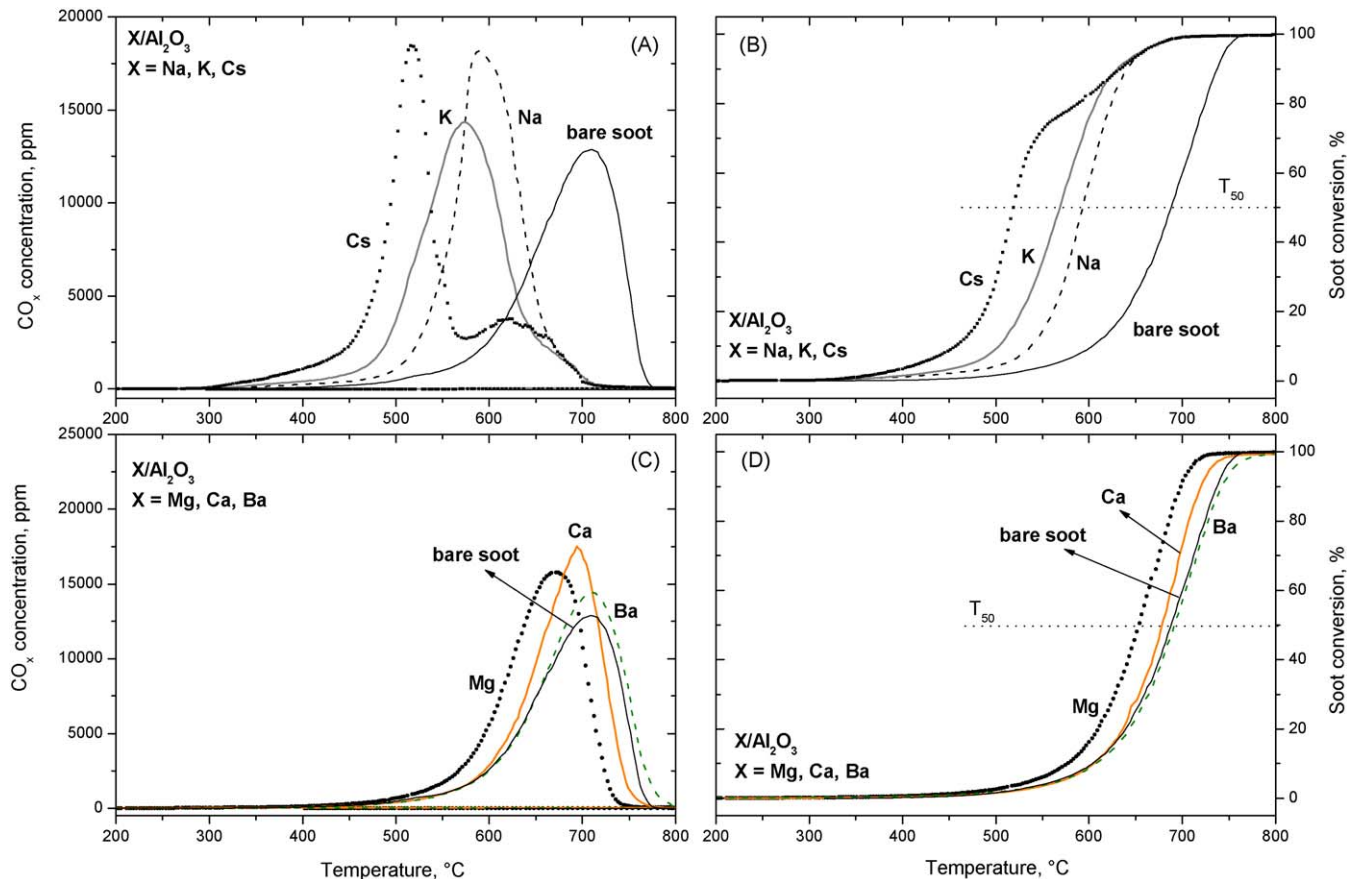


Fig. 3. Results of TPO experiments in O_2 (3% v/v) + He in terms of CO_x concentration (A and C) and in terms of soot conversion (B and D) over loose contact systems.

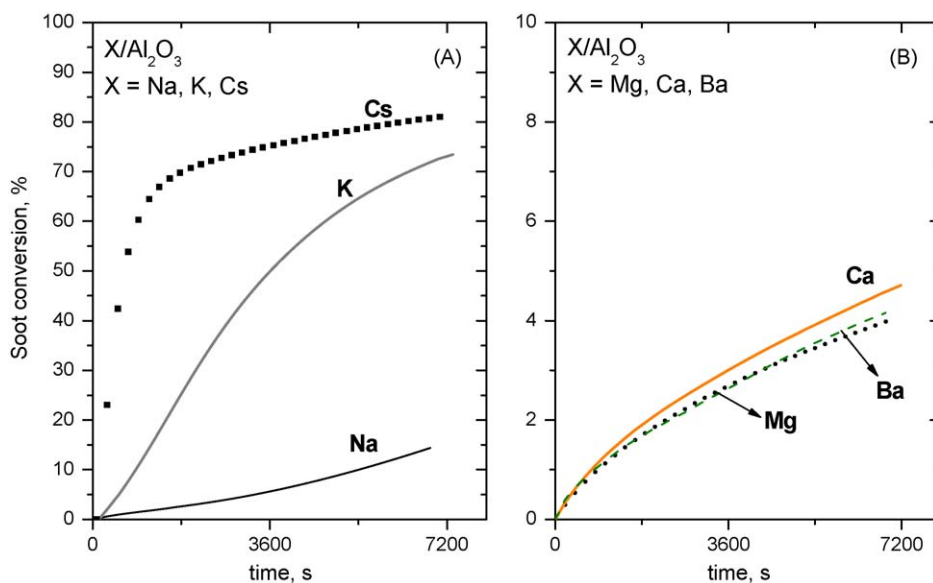


Fig. 4. Results of isothermal oxidation in presence of O₂ (3% v/v) + H₂O (1% v/v) + He in terms of soot conversion over loose contact systems: (A) alkaline metal oxide; (B) alkaline-earth metal oxide.

In the case of alkaline-earth oxides (Fig. 2B) the catalytic activity for soot combustion follows the order Ba \gg Ca \gg Mg, and after 1 h the soot conversion approaches 78%, 25% and 5%, respectively. These results are in line with TPO data showing the high activity of the Ba-doped system, and the poor activity of the Mg-doped system.

4.2. Loose contact systems

The reactivity of soot with the same catalytic elements has also been investigated under loose contact conditions for comparison purpose. These conditions have been obtained by gently mixing the soot and catalyst powders in a vial, and might be considered representative of the soot/catalyst contact in a catalytic filter.

Fig. 3A and C show the results of TPO experiments carried out in the case of the alumina supported alkaline and alkaline-earth oxides mixed with soot, respectively. The results obtained in the case un-catalyzed soot oxidation are also shown for comparison purposes. Fig. 3B and D show the results obtained during the TPO experiments in terms of soot conversion.

The alumina supported alkaline-earth oxides (Fig. 3C and D) show a very poor reactivity in the soot oxidation. The presence of the catalyst samples does not appreciably affect the temperature onset of the soot oxidation, but it results in higher CO₂ selectivities if compared to the un-catalyzed soot oxidation. CO₂ selectivity near 84%, 72% and 92% are measured in the case of the Ba/Al₂O₃, Ca/Al₂O₃ and Mg/Al₂O₃ samples, respectively.

Different results have been obtained in the case of the alkaline containing samples (i.e. Na/Al₂O₃, K/Al₂O₃ and Cs/Al₂O₃, Fig. 3A and B), since the presence of these catalyst samples significantly enhances the combustion of soot with respect to the alkaline-earth oxides (compare Fig. 3A and C). In particular for the Na-based catalyst the onset temperature for soot oxidation is near 420 °C, i.e. about 60 °C below that of the bare soot. In the case of the K/Al₂O₃ and Cs/Al₂O₃ samples a further increase in the reactivity is observed: the ignition temperatures decrease down to 370 °C and 320 °C, respectively. This also leads to a decrease in the maximum peak temperature (T_{\max} = 570 °C and 515 °C, respectively).

In all cases, a high selectivity to CO₂ is observed: values of 85%, 98% and 92% are measured for the Na/Al₂O₃, K/Al₂O₃ and Cs/Al₂O₃ samples, respectively.

Finally, soot oxidation tests under isothermal conditions have also been performed in the case of alkaline and alkaline-earth oxide-based catalysts in loose contact with soot, and results are shown in Fig. 4. In line with the results of TPO experiments, soot oxidation occurs very slowly in the case of the alkaline-earth oxides catalysts (Fig. 4B). In fact after 1 h soot conversion approaches 2–3% in all cases. A different behaviour is apparent in the case of the alumina-supported alkaline samples (Fig. 4A). In this case it clearly appears that soot oxidation is faster than in the case of the alkaline-earth samples. The catalytic activity for soot combustion follows the order Cs \gg K \gg Na; after 1 h the soot conversion approaches 75%, 50% and 5% over Cs/Al₂O₃, K/Al₂O₃ and Na/Al₂O₃ catalyst samples, respectively.

5. Discussion

In this work a systematic study on the reactivity of selected alkaline (Na, K, Cs) and alkaline-earth (Ca, Ba, Mg) oxide catalysts in the oxidation of a model soot sample (Printex U) has been performed, with the aim of obtaining informations about the intrinsic reactivity of these catalytic elements. For this purpose samples in which the active elements have been directly deposited on the soot have been prepared (“full contact” conditions). In this way the activity in the combustion of soot of the various elements is monitored under very intimate contact conditions: being the obtained results not controlled by the catalyst/soot contact, they are representative of the true reactivity of the active species.

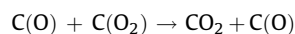
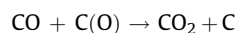
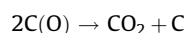
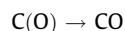
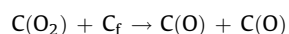
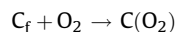
From the data presented above it appears that under these “full contact” conditions the combustion of soot is greatly enhanced in the presence of either alkaline or alkaline-earth oxides. Indeed in all cases a significant increase in the soot oxidation activity with respect to the un-catalyzed soot combustion has been observed, with the only exception of Mg for which a negligible effect has been monitored.

Although many literature studies have pointed out the noticeable promotion of alkalis for the soot combustion in various oxides-based catalysts [see e.g. Refs. 6–9], rather few data are reported in the literature on the role of alkaline-earth metal oxides [27]. Besides, systematic studies on the intrinsic reactivity of these compounds are rather scarce. Noteworthy, the results presented in this work point out that alkaline and alkaline-earth

metal compounds exhibit by themselves a significant catalytic activity in the soot oxidation reaction, even in the absence of other components. In fact the TPO and isothermal experiments data previously reported indicated that all the investigated alkalis are very active in the combustion of soot (the following order of reactivity is apparent: $\text{Cs} \geq \text{K} > \text{Na}$), whereas differences are observed in the reactivity of the selected alkaline-earth oxides. For these species the following order of reactivity is apparent: $\text{Ba} > \text{Ca} \gg \text{Mg}$, with Mg being poorly reactive in the soot oxidation. The performances of the most active elements (i.e. Cs and K) are noteworthy, being even higher than that of noble metals (e.g. Pt). In fact TPO experiments (herein not shown) carried out with Pt/soot samples pointed out that the activity of Pt in the soot oxidation is lower than that of the most reactive alkaline and alkaline-earth oxides used in this study.

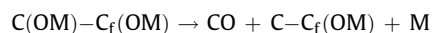
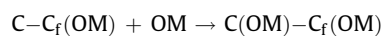
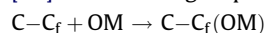
Moreover, the presence of both alkaline and alkaline-earth elements also promotes the CO_2 selectivity with respect to the uncatalyzed soot oxidation. In fact the CO_2 selectivity for the uncatalyzed combustion process is near 50–60%, in line with other reports [1,4], while in the presence of the alkaline and alkaline-earth compounds (with the only exception of Mg) the CO_2 selectivity exceeds 90%. The very high reactivity of alkaline and alkaline-earth oxides in soot combustion can be conveniently exploited, in principle, in Fuel Borne Catalyst (FBC) applications, as indeed claimed in the technical literature [28].

From the data reported above, it is clear that the alkaline and the alkaline-earth oxides are involved in some of the steps of soot oxidation by oxygen. The mechanisms involved in the reaction of oxygen with solid carbon have been extensively studied in the literature, although several aspects have not been clarified so far. It has been suggested [1,4] that non-catalytic soot oxidation occurs via the involvement of chemisorbed molecular oxygen which reacts with carbon sites according to the following reaction scheme:



where C_f is a free carbon site available for oxygen chemisorption, $\text{C}(\text{O}_2)$ the chemisorbed molecular oxygen species and $\text{C}(\text{O})$ a stable oxide surface species. This mechanism provides for both CO and CO_2 formation as primary products; under non-catalytic condition the CO/ CO_2 ratio is dependent on the supply of oxygen and on the temperature but is mostly in the order of unity, as indeed observed in our experiments in the case of the bare soot.

As reported above, the observed beneficial role of alkali metal compounds (and, to minor extent, of alkaline-earth metal compounds) in the C oxidation is well recognized although mechanistic indications are rather scarce. Mechanisms based on different oxygenated intermediate species such as carbonate, metal oxide, superoxide, phenolate groups, have been proposed [29–34]. Based on both theoretical [35] and experimental studies [36] the following sequence has been proposed:



where C_f is a free carbon site available for oxygen chemisorption, OM and M represent a non-stoichiometric alkaline oxygenated

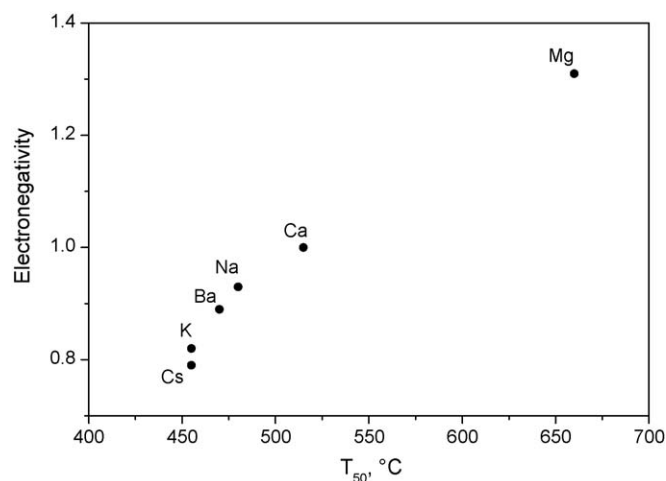


Fig. 5. Correlation between full contact systems combustion activity (in terms of T_{50}) and their electronegativity.

compound and its reduced form, respectively. The role of alkali compounds in this oxygen-transfer mechanism is ascribed to their electron-donating effect which increases the local electron density of neighboring C carbon sites promoting their affinity for binding an oxygen atom. As a consequence, this leads to substantial weakening of the C–C_f bonds and thus promotes the carbon gasification process.

According to the mechanistic indications discussed above, it is expected an increase in the catalytic activity with the electropositivity of the alkali metals. Accordingly, a correlation has been searched between the reactivity in the soot combustion (represented e.g. by T_{50}) and the electronegativity of the investigated metal ions. As shown in Fig. 5, in which the values of electronegativity are plotted as a function of T_{50} of the selected metal ions, a clear correlation is in fact apparent between electronegativity and activity in the soot combustion under full contact conditions, with the overall activity ranking ($\text{Cs} \geq \text{K} > \text{Ba} > \text{Na} > \text{Ca} \gg \text{Mg}$) which follows the electropositivity order of the investigated elements. The same trend is apparent if other catalytic activity indexes are considered, based both on isothermal conversion data and on TPO runs (e.g. T_{on} , in this case with the only inversion in the reactivity of Ba and Na).

Notably, the same reactivity order of alkaline oxides (i.e. $\text{Cs} > \text{K} > \text{Na}$) has been pointed out in the catalytic oxidation of soot by Shangguan et al. [6] and by Neeft et al. [37]. Saracco et al. [38] attributed the higher reactivity of Cs-vanadate catalyst than K-containing ones to the greater electropositivity of Cs vs. K. Also Aneggi et al. [39], investigating alkali promoted ceria based catalysts, suggested that the order of activity in soot oxidation ($\text{Cs} > \text{Rb} \approx \text{K} > \text{Na}$) depends on the electronegativity of the alkaline metal ion. Among the alkaline-earth metals, Radovic et al. [40] suggested the same order of reactivity observed in this study, i.e. $\text{Ba} > \text{Ca} > \text{Mg}$, and related this ranking to the aptitude of the selected elements to the peroxide and/or superoxide formation.

Notably, when considering the loose contact systems the correlation between electropositivity and activity in the soot combustion is no more apparent. This indicates that under these conditions other parameters play a role in the activity. In particular Ba and Ca show a very poor reactivity under loose conditions, although their reactivity under full contact conditions is remarkable. This indicates that under loose contact conditions the reactivity of these species is limited by the efficiency of the contact between soot and the active sites.

On the other hand alkaline-based catalysts show remarkable soot oxidation activity even under loose contact conditions,

although it is lower if compared to the analogous full contact samples. In fact Cs/Al₂O₃, K/Al₂O₃ and Na/Al₂O₃ samples show a significant decrease in the soot ignition temperature with respect to the bare soot, from 480 °C down to 320, 370 and 420 °C for Cs/, K/ and Na/Al₂O₃, respectively. Although less active than the corresponding full contact samples, the reactivity of these catalysts is noteworthy, being even higher than that of noble metal based samples (i.e. Pt) supported on the same alumina support [21].

In line with literature reports [2,3], it is speculated that under loose contact conditions the alkaline-containing samples maintain a high reactivity due to the mobility of the alkaline compounds on the alumina surface. In fact several authors ascribe the catalytic role of alkalis present in various oxide catalysts formulations to the formation of low melting point compounds, or of eutectics with other components of the catalyst. This would improve the surface mobility of the active species and hence the soot–catalyst contact, which is considered a limiting factor in the catalytic combustion of soot [2,3,12–14,16,22,23,41]. A migration of the active elements from the catalysts surface to the soot particles has also been suggested in the case of K-containing samples [16]. In our samples the nature of the alkaline surface compounds (oxide, hydroxide, carbonate, etc.) involved in the reaction is not known, although the presence of carbonates and/or bicarbonates is likely. Some of these species may possess high surface mobility. Along similar lines, the poor performances seen in the case of the investigated alkaline-earth metal oxide catalyst under loose contact conditions suggests that the reactivity of these samples is limited by the efficiency of the soot-active site contact, i.e. by the poor mobility of the active surface species. In fact Ba and Ca exhibit a noticeable intrinsic activity under full contact conditions. These results are in line with the conclusions of Neeft et al. [2,3] who correlated the low activity of Ca, Ba and Mg metal oxide catalysts in loose contact with soot to the scarce mobility of these catalytic species. However these aspects need to be further clarified and investigation are presently ongoing in our labs.

It is noted that being characterized by high surface mobility, alkaline metal oxides based catalysts have been claimed to suffer for the loss of the active elements. In fact several studies have been carried out on stability of alkaline-based catalyst, in particular K-based catalysts [16,39,42,43], and these studies pointed out that potassium-containing catalysts may deactivate under severe hydrothermal aging, due to the sublimation of potassium [16,39]. On the other hand, other literature studies point out the active K component can be stabilized on the catalyst surface. For instance Jimenez et al. [42] investigated the combustion activity of K/MgO catalysts, and showed that the activity of the catalysts was kept constant during isothermal cycles. Moreover it must be mentioned that the recent developments of the DPNR system are based on several catalytic formulations including potassium as well [44].

We have recently analyzed the capacity of the same K/Al₂O₃ catalyst used in this study to participate in consecutive isothermal cycles (limited at 400 °C) while maintaining its activity [21]. A significant decrease in the combustion activity has been indeed noticed passing from the first to the second isothermal cycle, then the catalyst activity becomes stable. These aspects are currently under investigations in our labs, including the resistance of the catalyst to repeated water washing procedures.

6. Conclusions

The reactivity of selected alkaline (Na, K, Cs) and alkaline-earth (Ca, Ba, Mg) oxide catalysts in the oxidation of a model soot sample (Printex U) has been investigated in this study. With the aim of obtaining information about the intrinsic reactivity of the selected catalytic elements, catalyzed soot samples have been prepared in

which the active species have been directly deposited on the soot (“full contact” conditions). Hence by avoiding any influence of the type of contact, the intrinsic reactivity of the selected elements could be evaluated.

It has been found that the combustion of soot is greatly enhanced by the presence of either alkaline or alkaline-earth oxides, with Cs and Mg exhibiting the highest and the lowest activity, respectively. The reactivity in the soot combustion of the selected elements well correlate with the electropositivity of the investigated metal ions, in line with literature mechanistic proposals for the soot oxidation pointing out the relevance of the electron-donor characteristics of the active elements.

The correlation between electropositivity and activity in the soot combustion is however not apparent when a “full contact” is not guaranteed between the catalytic elements and the soot, e.g. under loose contact conditions. Under these conditions the reactivity of alkaline compounds is still remarkable, whereas that of the alkaline-earth compounds is very poor. It has been suggested that under these conditions the catalytic activity is governed by other factors, and particularly by the mobility of the surface species which favors the soot–catalyst contact and hence the reactivity. Although a precise knowledge of the nature of the catalytic species involved in the soot oxidation (oxide, hydroxide, etc.) is not known, the poor performances observed in the case of the alkaline-earth metal oxides may suggest for these elements a poor mobility of the active surface species, as opposite to alkaline oxide based catalysts which show a high reactivity even under loose contact conditions.

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